re-BUS

You have downloaded a document from
RE-BUŚ
repository of the University of Silesia in Katowice

Title: The Mossbauer and x-ray studies of the spinel ferrites Cu0.5Fe0.8Cr2Se4 prepared by the ceramic method

Author: Ewa Maciążek, Aneta Hanc, Rafał Sitko, Beata Zawisza, Izabela Jendrzejewska, Janusz Mrzigod

Citation style: Maciążek Ewa, Hanc Aneta, Sitko Rafał, Zawisza Beata, Jendrzejewska Izabela, Mrzigod Janusz. (2008). The Mossbauer and x-ray studies of the spinel ferrites Cu0.5Fe0.8Cr2Se4 prepared by the ceramic method. "Acta Physica Polonica A" (Vol. 114, nr 6 (2008), s. 1599-1603).

Uznanie autorstwa - Użycie niekomercyjne - Bez utworów zależnych Polska - Licencja ta zezwala na rozpowszechnianie, przedstawianie i wykonywanie utworu jedynie w celach niekomercyjnych oraz pod warunkiem zachowania go w oryginalnej postaci (nie tworzenia utworów zależnych).

UNIWERSYTET ŚLĄSKI W KATOWICACH
Biblioteka Uniwersytetu Śląskiego
Ministerstwo Nauki i Szkolnictwa Wyższego

Proceedings of the Polish Mössbauer Community Meeting 2008

The Mössbauer and X-Ray Studies of the Spinel Ferrites $Cu_{0.5}Fe_{0.5}Cr_2Se_4$ and $Cu_{0.2}Fe_{0.8}Cr_2Se_4$ Prepared by the Ceramic Method

E. Maciążek[a,*], A. Hanc[b], R. Sitko[a], B. Zawisza[a], I. Jendrzejewska[a] and J. Mrzigod[a]

[a]Institute of Chemistry, University of Silesia
Szkolna 9, 40-006 Katowice, Poland
[b]Institute of Materials Science, University of Silesia
Bankowa 12, 40-007 Katowice, Poland

Seleno-spinels with nominal chemical composition $Cu_{0.5}Fe_{0.5}Cr_2Se_4$ and $Cu_{0.2}Fe_{0.8}Cr_2Se_4$ were prepared as polycrystalline samples using ceramic method. The assumed composition was verified by wavelength-dispersive X-ray fluorescence spectrometry. The X-ray analysis was carried out in order to make phase analysis and to compare its results with those obtained with the Mössbauer spectroscopy.

PACS numbers: 61.05.cp, 61.66.Fn, 82.80.Ej, 75.50.Gg

1. Introduction

The synthesis of polycrystalline ferrites $Cu_{1-x}Fe_xCr_2Se_4$ has been described elsewhere [1]. The end members of this series exhibit different crystal structures. $CuCr_2Se_4$ crystallizes in spinel structure, space group $Fd\text{-}3m$ [2, 3]. It has a normal cation distribution, the copper ions being located at the tetrahedral interstitial sites of the selenium sublattice, and chromium ions at the octahedral ones. The lattice parameter is equal to 1033.76 pm. $FeCr_2Se_4$ crystallizes in the monoclinic structure, space group $I\frac{2}{m}$; where both iron and chromium occupy octahedral sites in the selenium array [4].

Attempts to substitute copper by iron were undertaken in this paper. X-ray and Mössbauer spectroscopy analyses were carried out in order to make phase analysis. It was established that iron ions were located in two different interstitials. The oxidation state of iron was confirmed. The occurrence of a spinel phase as a non-magnetic one acknowledged the formation of a low-spin complex.

*corresponding author; e-mail: emaciazek@ich.us.edu.pl

2. Experimental procedure

2.1. Samples preparation

The spinel ferrites were obtained using the ceramic method. As the starting materials, the stoichiometric amounts of metal selenides: CuSe, Cr_2Se_3, and FeSe were used.

The samples were obtained from the binary selenides: CuSe, Cr_2Se_3, and FeSe. The ceramic method was used. Stages of the process were as follows:

- the stoichiometric amounts of binary selenides were weighed and put in quartz ampoules,
- ampoules were evacuated to 10^{-5} Torr and sealed,
- samples were sintered in annealing furnace for six days: first day at 573 K, second day at 873 K and the following days at 1073 K,
- ampoules were opened, samples were pulverized in an agate mortar, sealed in quartz ampoules and sintered again using temperature of 1273 K at the last step.

Then, the obtained quaternary compounds were subjected to phase analysis using X-ray powder diffraction method. X-ray diffraction (XRD) patterns were collected using Siemens D5000 diffractometer and Cu K_α radiation. The data stored in JCPDS catalogue were used in order to identify spinel and other phases. As the obtained samples occurred multi-phase, the third annealing procedure in temperature of 1273 K and quenching was applied in order to obtain single phase compounds. The X-ray phase analysis was repeated and lattice parameters were determined by the computer program HX 61S [5].

2.2. Analytical measurements

The chemical composition of polycrystalline samples was determined by wavelength-dispersive X-ray fluorescence spectrometry (WDXRF). The material was weighed on a micro-analytical balance in amounts of 25 mg. Then the material was etched in 1 mL of concentrated nitric acid and 3 mL of hydrochloric acid. The solution was transferred into 25 mL volumetric flask and filled up to the mark with water. Then 0.5 mL of the solution was pipetted onto the Millipore filter, dried and measured by WDXRF. The quantitative analysis was performed using several multielement standards. Measurement conditions: side-window silver target X-ray tube operated at 50 kV and 40 mA; LiF(200) analyzing crystal; vacuum; K_α lines; flow-proportional counter (counter gas 90% Ar + 10% CH_4) for Cr and Fe, flow-proportional counter and scintillation counter for Cu and Se.

2.3. The Mössbauer spectroscopy

The measurements of the ^{57}Fe Mössbauer spectra were performed in transmission geometry by means of a constant spectrometer of the standard design. The 14.4 keV gamma rays were provided by a 50 mCi source of ^{57}Co/Rh. The spectra were measured at room temperature. The selected obtained spectra are presented

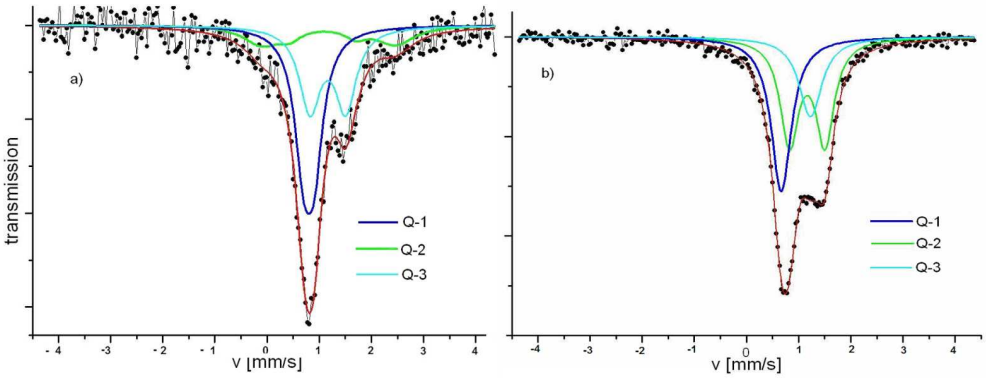

Fig. 1. The ^{57}Fe Mössbauer transmission spectra for (a) $Cu_{0.53}Fe_{0.54}Cr_{2.05}Se_4$ and (b) $Cu_{0.19}Fe_{0.82}Cr_{2.02}Se_4$.

in Fig. 1. Hyperfine parameters of the investigated spectra were related to the α-Fe standard. Experimental spectrum shape was described with a transmission integral calculated according to the numerical Gauss–Legendre procedure.

In the Mössbauer effect investigations the samples were prepared in the form of pellets with Li_2CO_3 as a binder, in which the investigated material was placed uniformly. The uniformity of samples was confirmed using optical microscope.

3. Results and discussion

Based on the X-ray analysis, the existence of the two phases — the spinel and the monoclinic one — was determined for both compounds. The $Cu_{0.2}Fe_{0.8}Cr_2Se_4$ compound was formed mainly in a monoclinic phase whereas $Cu_{0.5}Fe_{0.5}Cr_2Se_4$ — in a spinel structure. Values of Miller's indices for monoclinic phase suggested space group $I\frac{2}{m}$ as for pure $FeCr_2Se_4$ (the other possibility is $C\frac{2}{m}$).

The increase in lattice parameters for spinel phase (Table I) with the increase in a doped iron is connected with bigger value of ferrous ionic radius in tetrahedral coordination than that of copper: $r_{Fe} = 77$ pm, $r_{Cu} = 71$ pm [6].

The Mössbauer spectroscopy also confirms the occurrence of two phases: the magnetic (connected with monoclinic structure) and non-magnetic (corresponding to spinel) one in both samples. The non-magnetic phase was described by unresolved quadrupole lines (Q-1). The magnetic phase was characterized by two components (Q-2 and Q-3) described as doublet of lines (which approximates an unresolved Zeeman sextet) corresponding to the change of local surroundings of the Mössbauer nuclide.

The non-magnetic line on $Cu_{0.5}Fe_{0.5}Cr_2Se_4$ spectra is much stronger than in spectra of $Cu_{0.2}Fe_{0.8}Cr_2Se_4$ which is in good agreement with the X-ray analysis where similar quantitative distribution between these two phases was established. The non-magnetic behavior of ferrous ions in spinel constituent confirms the formation of a low-spin complex.

TABLE I

The chemical composition, phase analysis and lattice parameters.

The nominal chemical composition	The obtained chemical composition	Phase analysis and lattice parameters [pm]
$Cu_{0.5}Fe_{0.5}Cr_2Se_4$	$Cu_{0.53}Fe_{0.54}Cr_2Se_4$	spinel $a_0 = 1037.88$, traces of monoclinic phase $a_0 = 627.15, b_0 = 362.27$, $c_0 = 1185.84, \beta = 90.92^\circ$
$Cu_{0.2}Fe_{0.8}Cr_2Se_4$	$Cu_{0.19}Fe_{0.82}Cr_{2.02}Se_4$	monoclinic phase, $a_0 = 627.64, b_0 = 362.59$, $c_0 = 1185.87, \beta = 90.92^\circ$, spinel $a_0 = 1039.75$

The presence of Q-2 and Q-3 components was connected with the spinel structure but different further neighborhoods. Some excess of cations confirmed by analytical measurements could occupy extra sites in the selenium array [7] which could cause different interactions of iron.

TABLE II

Hyperfine parameters: isomer shift (IS) and quadrupole splitting (QS) and A — subspectral area of the investigated samples.

The obtained chemical composition	Component	IS* [mm/s] ±0.005 (mm/s)	QS [mm/s] ±0.005 (mm/s)	A [%] ±2 (%)
$Cu_{0.53}Fe_{0.54}Cr_{2.05}Se_4$	Q-1	0.28	0.24	68
	Q-2	0.38	0.48	13
	Q-3	0.41	0.15	19
$Cu_{0.19}Fe_{0.82}Cr_{2.02}Se_4$	Q-1	0.21	0.23	37
	Q- 2	0.32	0.31	27
	Q-3	1.20	0.11	36

*Relative to the α-Fe foil at room temperature.

The values of hyperfine parameters (Table II, Fig. 1) pointed out the ferrous state in samples which was in good agreement with our preparation assumption.

4. Conclusions

Based on X-ray analysis and the results of the Mössbauer spectroscopy, the phase composition of the samples under study was determined. The existence of two phases: magnetic (connected with monoclinic structure) and non-magnetic

(corresponding to spinel) one in both samples was defined. The predominance of the non-magnetic phase was specified in the case of $Cu_{0.53}Fe_{0.54}Cr_{2.05}Se_4$, while in $Cu_{0.19}Fe_{0.82}Cr_2Se_4$ the magnetic component prevailed. The good compatibility of the results obtained from Mössbauer spectroscopy and XRD methods was received.

Acknowledgments

The X-ray measurements were carried out at the Department of Solid State Physics, Institute of Physics, University of Silesia. The present work is funded from science resources for years 2008–2010 as research projects No. N N204 289134 (2891/B/H03/2008/34) and N N204 1784 33 (1784/B/H03/2007/33).

References

[1] H.N. Ok, Y. Chung, *Phys. Rev. B* **20**, 4550 (1979).

[2] I. Okońska-Kozłowska, J. Kopyczok, H.D. Lutz, Th. Stingl, *Acta Crystallogr. C* **49**, 1448 (1993).

[3] H. von Philipsborn, *J. Cryst. Growth* **9**, 296 (1971).

[4] L. Morris, P. Russo, A. Wold, *J. Phys. Chem. Solids* **31**, 635 (1970).

[5] F. Ahmed, *Instruction to Cell Dimension Program HS60s*, Loughborough University, unpublished results.

[6] R.D. Shannon, *Acta Crystallogr. A* **32**, 751 (1976).

[7] A. Payer, R. Schöllhorn, *J. Alloys. Comp.* **191**, 37 (1993).